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On the complex H-bonding network in paravauxite, $Fe^{2+}Al_2(PO_4)_2(OH)_2 \cdot 8\,H_2O$

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Phosphate minerals represent the major host for transition metals and H_2O in pegmatitic rocks, playing an essential geochemical role in the evolution processes of pegmatites. A good knowledge of their crystal chemistry is therefore necessary to better understand the genesis of pegmatites. Paravauxite is a mineral found in hydrothermal tin veins and granite pegmatites [1,2]. Its ideal chemical formula is $Fe^{2+}Al_2(PO_4)_2(OH)_2 \cdot 8H_2O$. Its crystal structure was solved and refined by Baur [3] in 1969 on the basis of single-crystal X-ray diffraction data. This structure model appears to be consistent. However, due to the technical limitations of X-ray diffraction, the refinement only provided the isotropic displacement parameters, and the positions of nine independent proton sites were assigned but not refined. This led to a poor description of (the expected) complex H-bonding scheme in the paravauxite structure. In light of this, the crystal structure of a natural paravauxite was reinvestigated using electron microprobe analysis in wavelength dispersive mode (EPMA-WDS) and single-crystal neutron diffraction in an attempt to resolve these open questions.

Looking into a gem stone

A gemmy, pale green, single crystal of paravauxite (up to 9 mm in length and 5 mm in diameter) from the Siglo Veinte Mine, Bolivia, was used in this study. The determination of the chemical composition was performed by EPMA-WDS analysis on a polished crystal using a Jeol JXA-8200 microprobe with the following result:

$$^{Fe}(Fe^{2+}_{0.916}Mn^{2+}_{0.016}Mg_{0.064}Ca_{0.002})_{\Sigma 0.998}{}^{Al(1)Al(2)}Al_{2.005}\,{}^{P}(P_{1.998}Si_{0.002})_{\Sigma 2}O_8(OH)_2 \cdot 8H_2O.$$

A single-crystal neutron diffraction experiment was performed using the hot source (fast neutrons) single-crystal diffractometer HEiDi of the neutron source FRM II. The diffraction data were collected at 293 K with a wavelength of the incident beam of 1.1680(2) Å. The unit-cell parameters were refined on the basis of the 42 Bragg reflections (space group: P -1, a = 5.240(6) Å, b = 10.567(7) Å, c = 6.698(9) Å, α = 106.82(8)°, β = 110.77(9)°, γ = 72.23(9)°, V = 336.4(6) Å^3). A total number of 4190 reflections were collected up to $2\theta_{max}$ = 126.3° and sin(Θ)/λ = 0.76/Å, respectively. The discrepancy factor for the symmetry related reflections (based on Friedel pairs) was R_{int} = 0.0442. The anisotropic structure refinement was then performed using the SHELX-97 software [4], starting from the atomic coordinates of Baur [3] without H sites. The structure refinement was conducted with: *a)* the neutron scattering length of iron at the octahedral Fe site and the scattering length of aluminum at the octahedral Al(1) and Al(2) sites, also refining their site occupancy factors (*s.o.f.*); *b)* the scattering length of phosphorous at the tetrahedral P site, with full occupancy; *c)* the scattering length of oxygen at the OP(1), OP(2), OP(3), OP(4), OH(5), OW(6), OW(7), OW(8) and OW(9), with full site occupancies. Then, a structure model was implemented with nine H sites, (i.e., H(1), H(2), H(3), H(4), H(5), H(6), H(7), H(8) and H(9)) all at ~1 Å from the respective O sites. Given such a model, convergence was rapidly achieved. However, H(4) and H(9) showed unrealistically large displacement parameters, if compared to those of the other H sites. Further refinement cycles were then conducted splitting the H(4) and H(9) sites into two mutually exclusive sub-sites (*i.e.*, H(4A) and H(4B), H(9A) and H(9B)) only 0.4-0.6 Å apart. Their *s.o.f.* were not restrained. With this configuration, the refined displacement parameters had realistic values, convergence was achieved and the variance-covariance matrix showed no significant correlation among the refined parameters. No peak larger than

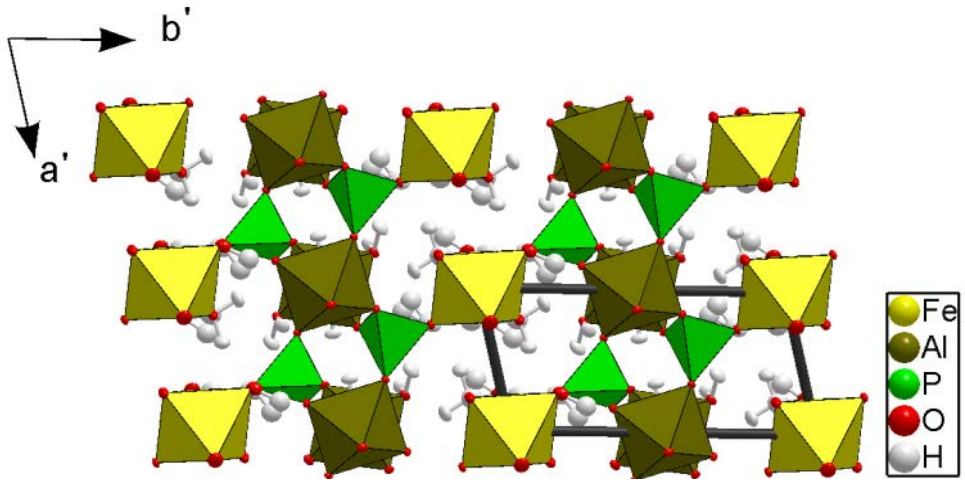

Figure 1: The crystal structure of paravauxite viewed down [001].

±1.3 fm/Å^3 was present in the final difference-Fourier map of the nuclear density. The final statistical index R_1 was 0.0495 for 194 refined parameters and 1678 unique reflections with $Fo > 4\sigma(Fo)$.

Locating the hydrogen in paravauxite

This is the first study in which the crystal structure of paravauxite has been investigated on the basis of single-crystal neutron diffraction. Previous structure data available in the literature [3] are based on single-crystal X-ray diffraction. The structural refinement of this study confirms the former general structure model [3]. The structure of paravauxite is composed of chains of corner-sharing Al-octahedra, running along [001], linked by P-tetrahedra to form layers parallel to the *ac*-plane. These layers are connected by Fe-octahedra (Fig. 1). Two independent Al-octahedra (*i.e.*, $AlO_4(OH)_2$ and $AlO_2(OH)_2(OH_2)_2$), one independent Fe-octahedron (*i.e.*, $FeO_4(OH_2)_2$) along with one independent PO_4-tetrahedron form the polyhedral "framework", and at least one independent "zeolitic" H_2O lies in the cavities.

Using the neutron scattering length of iron at the Fe site, the refined occupancy factor is *s.o.f.* = 0.921(7). This virtual partial site occupancy reflects the multi-elemental population at the Fe site, as shown by the EPMA-WDS [*i.e.*, with minor fractions of Mg (0.064 *a.p.f.u.*) and Mn (0.016 *a.p.f.u.*)]. The Al(1) and Al(2) sites were found to be fully occupied by aluminum (with refined *s.o.f.* = 1.02(2) and 1.05(2), respectively). The *s.o.f.* of the subsites H(4A) and H(4B), and H(9A) and H(9B) were refined without any restraint, and the sum [*s.o.f.*(H4A) + *s.o.f.*(H4B)] = 0.94(3) and [*s.o.f.*(H4A) + *s.o.f.*(H4B)] = 1.02(2) suggest full site occupancies within 2σ. The structure model with the sub-sites H(4A) and H(4B), and H(9A) and H(9B) is the best fit to the observed intensity data (at 293 K), with realistic displacement parameters.

The complex H-bonding scheme in the paravauxite structure is now well defined, with twelve independent H-bonds. Some of the H-bonds appear to be stronger than others. The weaker are characterized by low O-H···O angular values (i.e., 123 - 146°). Some H-bonds connect the Al-octahedra with the Fe-octahedra. The zeolitic H_2O molecule (*i.e.*, H(8)-OW(9)-H(9AB)) is connected via H-bonding to OP(1) (*i.e.*, the bridging oxygen between the Al(1)-octahedron and the P-tetrahedron), OP(3) (*i.e.*, the bridging oxygen between the Fe-octahedron and the P-tetrahedron) and OW(6) (*i.e.*, belonging to the Al(2)-octahedron). Further structural details are reported in [5].

[1] S. G. Gordon, Proc. Acad. Nat. Sci. Philadelphia 75, 261 (1922).
[2] S. G. Gordon, Proc. Acad. Nat. Sci. Philadelphia 96, 279 (1944).
[3] W. H. Baur, Neues Jahrbuch für Mineralogie Monatshefte 1969 430 (1969).
[4] G.M. Sheldrick, Acta Crystallogr. Sect. A 64, 112 (2008).
[5] G. D. Gatta et al., Mineralogical Magazine 78, 841 (2014).

Evaluation of Beam Time Proposals: Members of the Review Panels

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Figure 3: Members of the Review Panels from left to right (background): A. Radulecu, J. Neuhaus, O. Stockert, A. Ostermann, T. Nylander, K. Temst, A. Schneidewind, H. Ehrenberg, A. Senyshyn, W. Petry, S. Mattauch, C. Piochacz, A. Magerl, W. Sprengel, P. Schurtenberger. From left to right (foreground): F. Carsughi, P. Staron.

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Figure 4: First discussions among the referees during the welcome buffet for the review.

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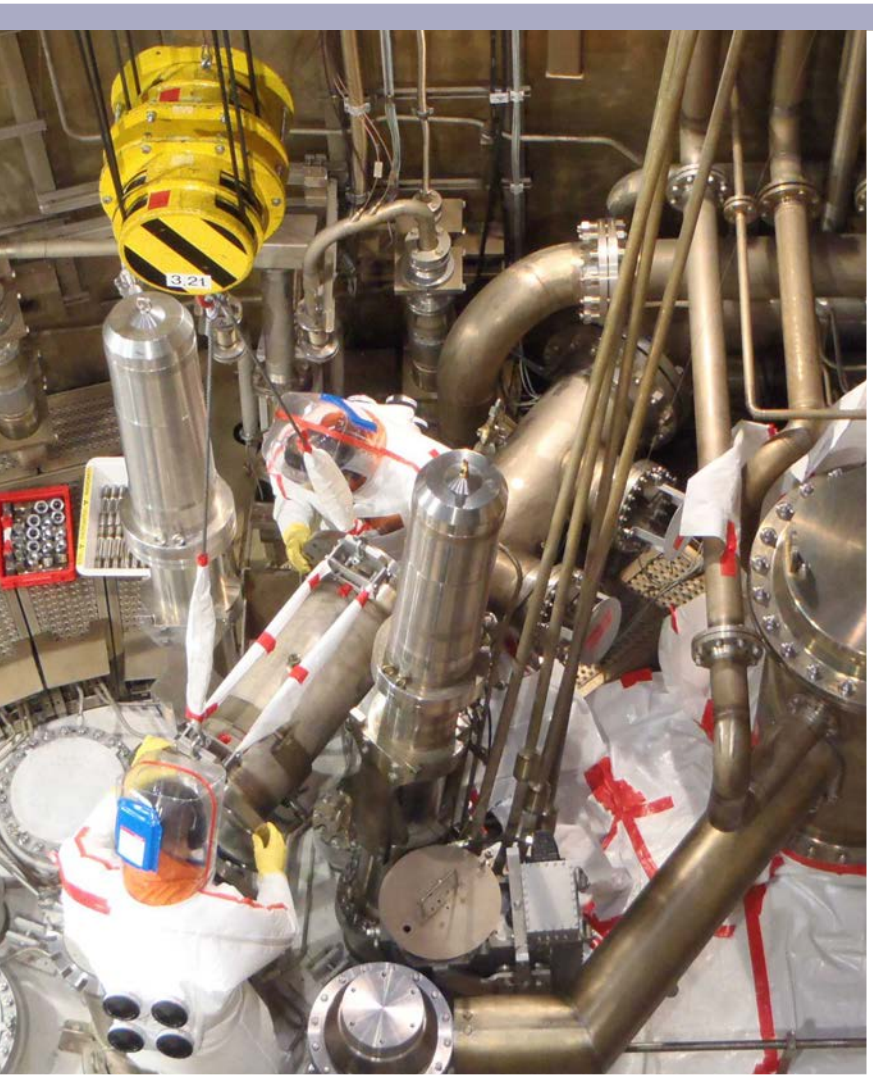

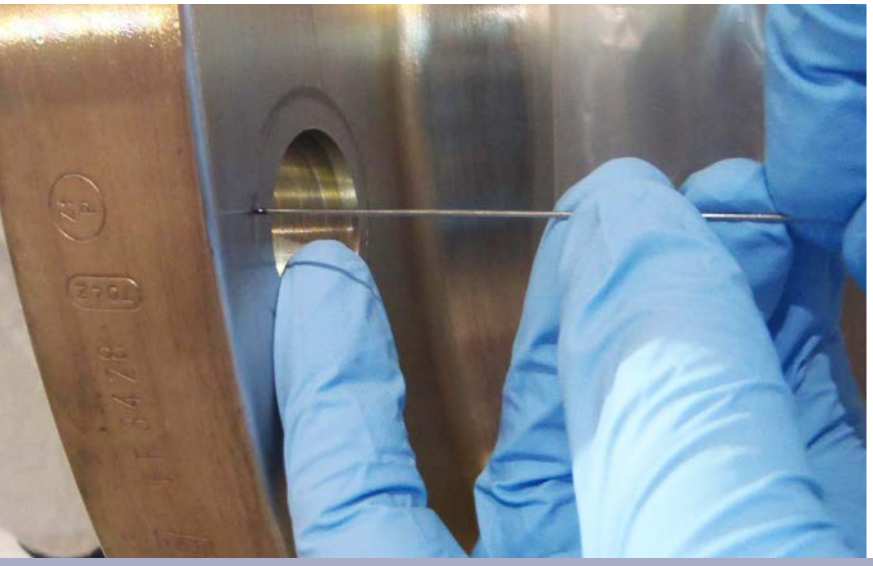

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